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# CHEMICAL RESEARCH, DEVELOPMENT & ENGINEERING CENTER

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# INFRARED WATER VAPOR CONTINUUM ABSORPTION: NEW ATMOSPHERIC ELECTRICAL MEASUREMENTS AND THEORY

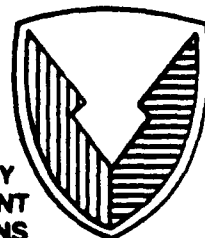Hugh R. Carlon
U.S. Army Fellow

RESEARCH DIRECTORATE

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The infrared (IR) continuum absorption, and probably similar absorption at longer wavelengths, can be attributed to populations of electrically-neutral water clusters that are present in near-Gaussian size distributions in water vapor and moist air. These neutral water clusters exist in equilibrium with much smaller populations of their water ions. Therefore, behavior of the ions and their equilibrium, IR-absorbing neutral clusters can be studied by careful measurements of the electrical conductivity of atmospheric moist air. Some results from a year of such measurements are presented and discussed. The most significant conclusions are (1) the vapor continuum absorption almost certainly is due to water clusters, (2) prime sources of such clusters include fine water droplets, and finely-structured water films on surfaces, at higher relative humidities (RH) in electric fields typical of those in the earth's atmosphere, (3) the variability of the continuum absorption arises from many factors, some of the most important of which are vapor RH, state of equilibrium, and fineness of droplets and surface water film structure; and (4) the continuum absorption at any wavelength is due only to those clusters of the distribution that absorb there, therefore, the total vapor cluster population cannot be estimated by — (continued on reverse)

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19. ABSTRACT (continued)

measurements at a single wavelength the extent of molecular clustering in water vapor may be far greater than previously supposed; most water molecules in the vapor might be clustered under conditions of energetic humidification with large populations of fine water droplets present.

PREFACE

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# CONTENTS

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# INFRARED WATER VAPOR CONTINUUM ABSORPTION:
## NEW ATMOSPHERIC ELECTRICAL MEASUREMENTS AND THEORY
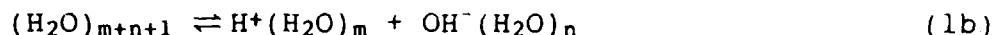
## 1. INTRODUCTION

Roberts et al.[1] have given a good description of the infrared (IR) water vapor continuum absorption. The continuum is manifest in the atmosphere as a continuous background absorption upon which are superimposed clearly-defined absorption lines that can be attributed to individual water molecules (monomers) in the vapor. The absorption at monomer lines is linearly dependent on water vapor partial pressure and has a positive temperature dependence. But the continuum absorption, which is most conveniently studied in atmospheric "window" regions (e.g., 8-13 μm where the monomers and other gases have little absorption), exhibits a quadratic dependence on water vapor partial pressure and a strong negative temperature dependence. These suggest that the continuum absorption arises from dimers and larger clusters of water molecules that exist in the vapor among a great preponderance of monomers.[2]

The absorbing cluster size distributions and populations depend upon vapor parameters including relative humidity (RH) or partial pressure and temperature.[3-5] The clusters always exist in equilibrium with small but proportional populations of water ions. Experiments show that the continuum absorption is proportional to the ion content or electrical conductivity of moist air,[5] and careful studies of vapor conductivity can reveal much about the sources of water clusters and the continuum absorption in the atmosphere. In 1987, the author completed a year of new research on the electrical conductivity of moist atmospheric air.[6] Results of this research and their important implications in our understanding of the IR continuum absorption are discussed in this report.

## 2. BACKGROUND

It has been known for many years that water fogs, especially when warm, exhibit far greater IR absorption and emission than can be explained by the absorption of monomers and optical scattering of droplets in moist air.[3] Measured emission spectra suddenly change shape and amplitude in response to small changes in ambient temperature and RH. This behavior also exists to a lesser extent in moist air that does not contain water droplets. The excess IR absorption cannot be explained by atmospheric constituents other than water, especially when measured in atmospheric "window" regions such as 8-13 μm.[3] Therefore, many authors have attributed this continuum absorption to clusters of water molecules or "water clusters."[2-5,7] The continuum absorption is characterized by

vague spectral features (rather than sharp lines), and its
absorption intensity can be extremely variable. Therefore, we
know that in the presence of finely divided liquid water sur-
faces such as droplets, the vapor contains IR-absorbing water
clusters. Because the continuum absorption intensity varies
proportionally with the measured water ion content of the
vapor,[5] we also know that equilibria exist between the water
clusters and ions; some examples include:

$$(H_2O)_n \pm e \rightleftharpoons (H_2O)_n\pm \tag{1a}$$

$$(H_2O)_{m+n+1} \rightleftharpoons H^+(H_2O)_m + OH^-(H_2O)_n \tag{1b}$$

or

$$HX(H_2O)n \rightleftharpoons H^+(H_2O)_n + X^- \tag{1c}$$

where $X^-$ can be a negative ion or an electron.

A typical distribution[4] for water ion clusters, from
moist air sampled at 20 °C and 60% RH, is shown in the Figure.
Compilations of large numbers of similar size distributions show
that the mean size $n_\mu$ of a distribution can be approximated by:

$$n_\mu \cong \sqrt{s}(0.44T_k - 119.12) \tag{2}$$

where $T_k$ is the Kelvin temperature, $s = \%$ RH/100, and the value
119.12 does not indicate high precision but instead serves for
many temperatures to round the mean cluster size to a whole
number. Water cluster size distributions in the vapor like that
in the Figure shift to the right with increasing RH and tempera-
ture at constant RH and to the left with decreasing RH and
temperature at constant RH.[4] Measurements of equilibrium
constants for reactions like those in equations 1a and 1b in
liquid water are routine and have been widely reported.[8-10]
Even the purest liquid water contains an equilibrium population
of ions at any temperature that is given by the so-called "ion
product," $K_w$. For example, at 25 °C, the population of positive
or negative ions in liquid water is $10^{-7}X$ that of the monomers
or neutral clusters (water is almost completely clustered by
hydrogen bonding at ambient temperatures).[11] Because $K_w$ is the
product of positive and negative ion concentrations, the total
ion population is a function of $\sqrt{K_w}$ that can be approximated by
a rewritten form of an equation of Holzapfel:[12]

$$\sqrt{K_w} \cong \exp(-4.085 - 3578/T_k) \tag{3}$$

8.

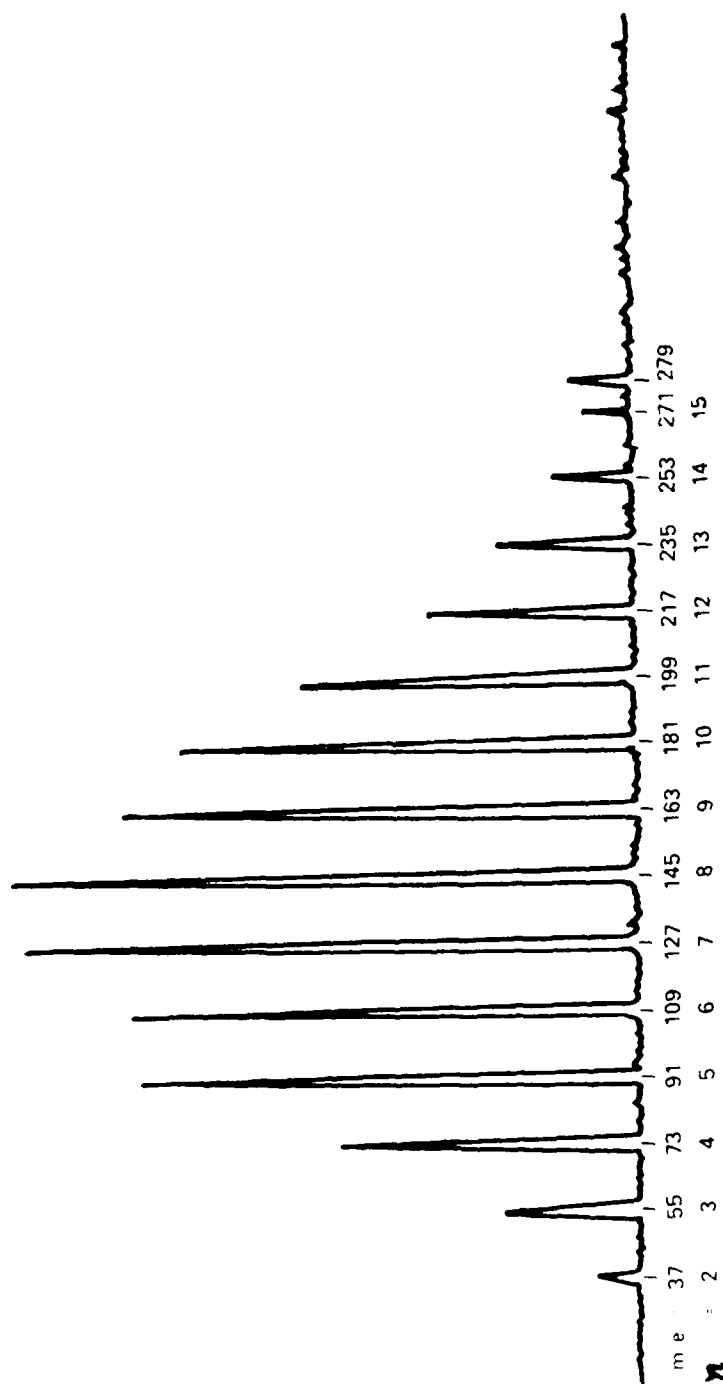# SPECTRUM OF 'CLEAN AIR' SHOWING REACTANT IONS H$^+$ (H2O)$_n$



Figure. Typical Size Distribution or Spectrum for Water Ion Clusters from "Clean" Moist Atmospheric Air Sampled at 20 °C and 60% RH. Such distributions exist for water ions and for much larger populations of neutral clusters in equilibrium with them (see text). The mean size of such distributions is approximated by equation 2 for a given RH and temperature.

Despite the fact that $\sqrt{K_w}$ is measured for pure liquid water, it has been known for many years that $\sqrt{K_w}$ gives an excellent approximation of the negative temperature dependence of the IR continuum absorption "self-broadening" coefficient $(C_s)_\lambda$ when corrected for water vapor partial pressure $p_w$ in the form:[9-13]

$$(\overset{o}{C_s})_\lambda = k\ \sqrt{K_w}/p_w \tag{4}$$

where k is a constant. In fact, equation 4 agrees closely[10] with the continuum absorption temperature correction equation derived empirically from the data of many spectroscopists by Roberts et al.[1] These results strongly suggest that a close link must exist between liquid water and the source of water clusters and ions involved in the vapor continuum absorption. But while $\sqrt{K_w}$ is measured by conductivity cell electrodes immersed in liquid water,[8] water ions in the vapor are measured by electrodes immersed in water vapor or in moist air. Clearly, some intermediate step must be involved to account for these results, and that step must involve the liquid/vapor interface, and possibly, the electric field applied to this interface (and to the liquid to measure $\sqrt{K_w}$). Accordingly, the author's research completed in 1987 was concentrated in these areas[6] and is reported below.

Other experimental data continue to be gathered from new measurements of many kinds. The case for dimers and larger water clusters as the explanation of the continuum absorption is stengthened by these new data although monomer theories based upon traditional line shapes continue to make this a contro- versial area of research.[2] A misconception that a continuum absorption explanation based on the water dimer must automati- cally exclude an explanation based on distributions of larger clusters in the vapor also seems to have evolved. The following brief discussion will show that this is not the case.

Suck et al.[14] have made a strong case for the water dimer as the cause of the continuum absorption near $\lambda = 10$ μm. Their arguments presume to rule out absorption by water clusters larger than the dimer because according to present theory, the larger clusters are not believed to exis in appreciable num- bers, except under conditions of vapor supersaturation[2] that would not be expected in the atmosphere. But this presumption fails to take into account the role of vapor equilibria between water ions and neutral clusters that do, in fact, result in the existence of huge populations of IR-absorbing neutral clusters in water vapor and moist air that are present in near-Gaussian size distributions (equation 1).

Experiments show clearly that the IR continuum absorp- tion is directly proportional to the water ion content of moist air, because the ion populations are directly proportional to much larger populations of IR-absorbing neutral clusters that

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are in equilibrium with them[5] (equations 1-4). The experimentally evaluated equation from simple oscillator theory for the wavelength of absorption of a cluster of "n" water molecules is:[5,9,13]

$$\lambda = 6.4 \ \sqrt{n}. \tag{5}$$

Therefore, $\lambda = 9.05$ µm for the water dimer (n = 2), $\lambda = 11.1$ µm for the water trimer (n = 3), etc. The continuum absorption at $\lambda \cong 10$ µm could be explained either as due to the dimer alone[14] or to the very smallest clusters (dimers, trimers, etc.) in a distribution of larger clusters in equilibrium with water ions (equation 1, Figure), or as arising from a combination of mechanisms in which case the continuum absorption behavior would be even more complex. The experimental (absorption) data would be the same near $\lambda = 10$ µm regardless of the cluster mechanisms involved. But existence of larger clusters also implies a great deal about the continuum absorption at longer wavelengths extending into the so-called "water vapor rotational region" where the variable absorption there is attributed only to modes of water monomers. A provocative finding is that simple calculations (using equation 5) and a neutral cluster size distribution (like that in the Figure) for water ions yield a shape for the continuum absorption spectrum[1] that closely matches experiment in the $\lambda = 10$–$30$ µm region. Furthermore, clusters of sizes up to n = 45 are measured in hot water vapor and steam.[4] Spectra calculated (equation 5) for these clusters closely match corrections originally suggested by Elsasser[15] to rationalize the use of vapor line models in explaining that the IR continuum absorption is due to distant wings of monomer lines in the rotational region. Elsasser used steam in his experiments in which large clusters were certain to be present. Water vapor or moist air above liquid water at temperatures above 43-50 °C always contain liquid droplets that are spontaneously nucleated on water clusters that reach the critical size n* ~ 45 for nucleation.[16]

There is evidence that the water cluster species responsible for the IR continuum absorption also absorb at wavelengths beyond the IR (e.g., in the millimeter waves); this would be consistent with the discussion in the previous paragraph. Gebbie[17] has described similar absorption in the millimeter waves, especially in fogs, attributable to water "polymers," in excess of that predicted by monomer and equilibrium dimer models; he noted that the variability of the phenomenon causes atmospheric observations to have poor reproducibility that has led some authors[18,19] to question the existence of excess or anomalous absorption and to suggest that experimental artifacts could explain such effects. Gebbie also discussed evidence for high values of ~ 1 eV in the exponent of a Boltzmann factor describing results where the dimer binding energy (due to a single hydrogen bond) would give ~ 0.2 eV. This

was attributed to large water clusters or polymers in the vapor. Although neutral water and ion clusters might exhibit reproducible, measureable vapor equilibria between themselves[5] (equation 1), it has not been understood until the present work how these equilibria relate even to such fundamental parameters as the partial pressure or the RH of moist atmospheric air. The populations of neutral water clusters and their equilibrium ions do not appear to depend solely upon ambient humidity, as previously assumed.

Roberts et al.[1] expected that their empirical equations would greatly improve predictive modeling of the IR continuum absorption, but variability of the absorption intensity has frustrated this expectation. Similarly, the author expected that his equations developed from cluster theory,[10] which closely resemble the equation of Roberts et al. (describing the temperature dependence of the continuum absorption), would find wide application. But experimental verification by other workers was not reported because of the variability of experimental data. Some data, like that of Montgomery,[20] gave unusual results explicable by cluster theory,[10] but no conclusions could be drawn. The author concentrated on cause-and-effect mechanisms involving water ions and clusters already present in the vapor,[21] believing that the cluster equilibria (equation 1) were related in simple ways to humidity and evaporation of liquid water. The new work[6] completed in 1987 and discussed below, has shown that the cluster-formation mechanism depends on fine water films including those deposited on surfaces in the atmosphere, but that bulk liquid water (as opposed to fine droplets) is not a significant source of water ions and neutral clusters in the vapor.

3.      EXPERIMENTAL CONSIDERATIONS, PROCEDURES, AND RESULTS

Details of the new experiments[6] are presented in Appendix A; interpretation of the new results is discussed in Appendix B and in the following sections of this report.

Briefly, the major problem faced in measuring electrical conductivity in water vapor or moist air, especially at high RH, is electrical leakage of the insulators supporting the cell electrodes. This is because the behavior of water ions that move under electric potentials in thin water films across moist insulator surfaces is much like that of water ions that leave moist cell electrodes and cross the vapor gap to be collected by other electrodes at different electrical potentials. Excellent insulators must be used if the vapor behavior is to be studied unequivocally. The author first approached this problem using several vapor conductivity cells of different electrode areas but identical insulator configurations.[9,22] The interpretation was that the measured water ions in moist air were produced by the decompos t. n of molecular complexes (water clusters) generated direc l/ by evaporation of liquid water according to

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equation 1.[23] Equilibria were shown to exist between water ions having near-Gaussian size distributions (Figure) and much greater populations of neutral clusters having similar size distributions,[24] because the ion charge lifetimes are a microsecond or less,[25] while neutral water clusters have "evaporation" lifetimes of seconds or longer. Therefore, in the vapor, neutral clusters can outnumber the ions with which they are in equilibrium at any instant of time by a factor of $> 10^7 X$, much like liquid water discussed for equations 3 and 4 above. Both the neutral and water ion clusters can have near-Gaussian size distributions like that in the Figure. The use of the ion product $K_w$ (equations 3 and 4) from liquid water to describe IR absorption by molecular clusters in water vapor was developed.[26] Further improvements in the design of vapor conductivity cells[27,28] with larger but lighter electrodes and much smaller insulators confirmed earlier results including the proportion- ality between water ion content and IR continuum absorption of moist air.[5] This led to the work[6] completed in 1987 in which cell insulator leakage was completely eliminated, and the source of water ions in the vapor was identified (described briefly in Appendix A).

This recent work, using moist air at atmospheric pres- sure, has led to several new findings that can be summarized as follows:

• When RH ≤50-60%, the number of water ions such as $(H_2O)_n^{\pm}$ (equation 1) in moist air is not large compared to other atmospheric ions that are produced by cosmic rays, radiation from the earth's crust, etc.[25] Under these conditions, total vapor ion populations per cubic centimeter are of the order $I_{cc} = 10^2 - 10^3$.[29] Therefore, the equilibrium population of neutral water clusters per cubic centimeter, $N_{cc}$ (equation 1), although much greater than $I_{cc}$, is still far outnumbered by the water monomer (vapor) populations, and the continuum absorption is moderate. Under these conditions, values of $I_{cc}$ measured with the author's conductivity cells[6,22-24,27-28] agree with those measured by standard instruments such as the Gerdien tube[30] and its later modifications.[29]

• As RH increases, thin water films are deposited upon surfaces immersed in the vapor. The thicknesses of these films are, under equilibrium conditions, directly proportional to RH. If two surfaces upon which water films have been deposited are at different electrical potentials [as for the cell electrodes (plates) in electric fields (Appendix A)], water ions will begin to pass through the air gap between the moist surfaces. This behavior has been observed even in electric fields as small as those that occur naturally in the earth's atmosphere during fair weather (0.5-1 V/cm). The measured conductivity current at a given RH is directly proportional to the electric field up to field strengths of several hundred volts per centimeter (i.e., Ohm's Law is obeyed). Many conventional instruments[29,30] cannot detect water ions because surface water films are not allowed to

form on their heated electrodes, because equilibrium cannot be established between the moist air aspirated through them and their electrodes or for other instrumental reasons.

- In a given electric field between two surfaces, the ion population and current passing through the air gap between the surfaces is strongly dependent upon RH, varying approximately as the thirteenth power of RH at higher humidities (Figure A-2) and as the seventh or eighth power at lower RH. This same range of dependence of $I_{cc}$ upon RH was measured and reported earlier (Figure 2 of reference 5), when it was shown to be directly proportional to the measured IR continuum absorption. This must indicate that the ability of thin water films on surfaces to produce water ions in electric fields depends strongly on the film thickness and "quality" that exists in equilibrium with the vapor as a function of RH. But the surface water films are "fragile," and unless they consist of finely divided water particles (fine droplets like those in fogs, etc.), water ions are not generated from them in significant numbers. For example, it was often observed in experiments[6] that if surface water films on the cell electrodes were disturbed so that they coalesced into bulk liquid water, the cell ion populations and currents fell precipitously by orders of magnitude. Measurements showed that although fine water droplets do, bulk liquid water does not produce ions, even in large electric fields, in significant numbers from its surface.

- As RH increases, the ion population $I_{cc}$ and the cell current increase rapidly but remain linear with the electric field up to field strengths of several hundred volts per centimeter (Figure A-3). In larger fields, molecular fragmentation occurs (equations 1b and 1c), and total ion production increases rapidly. Fields of 2 to 3 kV/cm are common (e.g., in thunderstorms).[29] When dehumidification occurs, data points frequently follow different loci than those in Figures A-2 and A-3 because equilibrium water films on surfaces do not always evaporate at the rates with which they were formed during humidification. Therefore, "Hysteresis-like" behavior is often observed in the ion content of air versus RH between moist surfaces; this is but one factor contributing to the variability of water ion and cluster populations between moist surfaces in moist air as RH changes.

## 4. DISCUSSION

These new experimental findings suggest that the variability observed in the IR continuum absorption can arise from many factors including:

a. The RH of ambient air or water vapor

b. The state of equilibrium between ambient air or water vapor at any RH and finely structured water films on surfaces, or fine water droplets in the vapor

c. The "quality" or fineness of water film or droplet structure (bulk liquid water produces essentially no ions)

d. "Hysteresis" effects in humidification versus dehumidification

e. The electric potential or field strength existing between surfaces or droplets in the vapor

f. The equilibria that continue to exist between water ions and neutral clusters (equation 1) when they are separated in space or time from the sources that produced them (e.g., the time constant of their interactions)

g. The interactions that occur between water ions, neutral clusters, and other atmospheric constituents, including gases and aerosols.[25,29]

The new experimental data[6] suggest that of these factors, a to c are most important, provided that even a small electric field exists (e). The latter factor might inadvertently be eliminated (e.g., in a steel-jacketed absorption cell in which no other source of water ion replenishment were provided). At RH <50-60% in the absence of fine water droplets or fine water films on surfaces, factors f and g are the only significant ones, and they contribute relatively little to the IR continuum. Therefore, the quadratic RH or partial pressure dependence of the continuum absorption probably arises from the relative inactivity of water clusters in the vapor at lower RH but their rapidly increasing activity at higher RH. In the latter case, when droplets are present in the vapor, the cluster absorption is often mistaken for optical scattering by the droplets as the source of measured IR attenuation. The role of collisionally induced water dimers[14] is unclear, but they are probably most significant at lower RH where larger water clusters are less populous and at temperatures approaching freezing. This complexity explains why the continuum absorption under typical atmospheric conditions has eluded understanding for such a long time. The molecular structure of water vapor changes drastically with RH and temperature. Under very moist and especially warm conditions, large clusters completely dominate the IR continuum absorption. If this is not totally understood, inappropriate experiments that produce very misleading results can be designed on the assumption that water vapor is a simple gas. For example, Elsasser[15] had no reason to suspect that ambient water vapor and steam are drastically dissimilar. Therefore, his use of steam data to apparently explain continuum absorption based on empirical monomer line wing models led to confusion that persists to the present day.

Atmospheric water ions can be studied using many techniques, including mass spectrometry[31] and measurements of the electrical conductivity of moist air (as discussed in this report). But neutral water clusters in the vapor are more difficult to study or even to detect. When a hydrogen-bonded neutral water cluster $(H_2O)_n$ reaches a size of only about n = 5 to 6, measurements by crossed-beam spectroscopy[32] show that its near-IR absorption spectrum already closely resembles liquid water. Castleman and his co-workers,[31] in extensive measurements of entropy and other thermodynamic properties of water ion clusters $H^+(H_2O)_n$, have found that clusters of size n = 4 to 6 or more are, thermodynamically, liquid water. Therefore, water clusters nearly 10 times smaller than the critical size $n* \sim 45$ needed for droplet nucleation[16] already behave like liquid "droplets" in the vapor and can impart to the vapor liquid-like behavior including IR continuum (and probably millimeter-wave) absorption and electrical properties as discussed here. For example, in the IR at $\lambda$ = 10 μm, the absorption coefficient per molecule of liquid water or per molecule bound into a water cluster is $10^3$ to $10^4$ times larger than this coefficient per molecule of water vapor (monomer) at this wavelength.[33] Larger neutral clusters have larger binding energies ($\sim$ 1 eV) than the water dimer ($\sim$ 0.2 eV)[17] due to the multiple hydrogen bonds that crosslink their molecules. When present, an ionic charge further increases the binding energy and stabilizes the cluster;[34] this also shifts the cluster absorption toward shorter wavelengths.

At present, there are only two practical ways in which the huge populations of neutral water clusters that are in equilibrium with their ions (equation 1) can be measured directly in water vapor or moist air sampled at atmospheric pressure. One way is by their IR continuum absorption as discussed in this report; but this interpretation is controversial[2] and cannot be "proven" except by the overwhelming weight of circumstantial evidence from many scientific disciplines. The other way is by adiabatically expanding a vapor sample in a cloud chamber to produce droplets that can be detected by optical scattering.[35] As the chamber is operated to successively higher expansions, the supersaturations achieved increase to values of s = % RH/100 = 4 to 5 or more. The droplets detected at highest supersaturations are nucleated first upon water ions like $(H_2O)_n'$, $H^+(H_2O)_m$, or $OH^-(H_2O)_n$ and, finally, upon the far more populous neutral clusters like $(H_2O)_n$ and $(H_2O)_{m+n+1}$ that are initially in equilibrium with the water ions (equation 1). From the very earliest cloud chamber studies of water, it has been found consistently that the ratio of neutral clusters to water ions in water vapor is larger than that inferred by the "ion product" measured for liquid water (equation 3).[8,12] For example, C.T.R. Wilson[36,37,4] found vast numbers of large, neutral water clusters per cubic centimeter of vapor ($N_{cc} > 10^8$) accompanied by much smaller populations of water ions per cubic centimeter ($I_{cc} < 10^2$). Physical limitations existed[38] on the maximum number of droplets nucleated from

clusters that Wilson could detect by optical means. Therefore, the true values of $N_{cc}$ could have been many orders of magnitude larger[4] than $N_{cc} \sim 10^8/cm^3$. Wilson's work was first carried out in 1897-1899 before hydrogen bonding was even known to exist; he did not understand the source of the huge neutral cluster populations ($N_{cc}$) but was adamant about the correctness of his results even to the point of suggesting that the known water molecule radius might be too small by a factor of 2 to 3.[36]

Therefore, even Wilson's earliest cloud chamber work, since confirmed by many other workers,[35] showed that in water vapor, the upper limit of the ratio $I_{cc}/N_{cc} = <10^2/>10^8 \sim 10^{-7}$ agrees with the measured ion product $K_w$ for liquid water at ambient temperatures. If the water ions are considered to be paried, then based on the experimental evidence, we can write for liquid water:[26]

$$(\text{liquid}) \quad I_{cc} \sim 2 \sqrt{K_w} \ N_{cc} \tag{6}$$

The similarity of behavior between water's liquid and vapor phase probably can be explained by the recent discovery[6] (as discussed in this report) that finely divided water droplets or surface films in electric fields are the source of water clusters (and their equilibrium ions) that give rise to the IR continuum absorption in the vapor. A good analogy can be drawn between the measurement of the ion product $K_w$ by application of a voltage between two small electrodes (plates) in liquid water, and the measurement of vapor ion conductivity by the application of a voltage between much larger plates (that compensate for phase density differences) at some RH, where the plates are coated by finely divided liquid water surface films. Therefore, the travel of electronic charges through a liquid water medium and the density-corrected medium liquid/vapor/liquid must be similar in some ways. Because a voltage must be applied to measure electrical conductivity, we cannot say for sure that liquid water is ionized except in an electric field. The ionization phenomena in the liquid, and between surfaces coated with fine water films in the vapor, might indeed be very similar in electric fields. We cannot even say for sure whether the known equilibria in equation 1 arises from liquid-like clusters leaving surface films and ionizing to a small extent in the electric field or by ions leaving the film in the electric field and subsequently attracting and clustering water monomers to form clusters.[29] The nature of the liquid water surface never has been understood. This physical interface between liquid water and its vapor, through which pass the species that determine such fundamental properties of water as its saturation vapor pressure, continues to elude description even by advanced techniques that work very well for simpler substances. Croxton[39] devotes a short chapter to the subject, after stating in a prologue that any **statistical-mechanical,** theoretical treatment of the water surface presents particularly formidable

problems and that such a discussion of these interfacial properties might well be "premature." DeBoer[40] states that if water's surface behavior was as expected from classical theory, many lakes and seas would evaporate in a few hours, and the oceans would be dry in a few days.

It was shown earlier that clusters in the vapor comprising 4 to 5 or more water molecules behave like liquid water. Therefore, liquid-like neutral water clusters can exist in the vapor, but the water ions in equilibrium with them should be far less populous than in liquid water simply because of the phase density difference. This suggests that, for the vapor phase, equation 6 should be corrected for phase density. Density corrections and other factors are considered in Appendix B, where sample calculations are presented using new data.[6]

The sample calculations in Appenidx B appear to support the hypotheses presented in this report. In particular, there is evidence that the extent of molecular clustering in water vapor may be far greater than previously supposed. If some maximum number of equilibrium ions (equation 1), and no more, can be produced at any temperature in saturated (100% RH) atmospheric air regardless of how energetic the humidification process is, few explanations would appear to exist other than that the neutral clusters in equilibrium with the measured ions comprise most of the water molecules in the vapor under these limiting conditions. But the IR continuum absorption at any wavelength would still be limited to those clusters of corresponding size in the distribution (equation 5). Therefore, inferences that the total population of all clusters in the vapor can be deduced by IR absorption measurements at a single wavelength (e.g., as attributed to the water dimer at $\lambda \sim 10$ μm)[14] are extremely risky.


5.      CONCLUSIONS

The new research[6] (completed in 1987) into the electrical properties of moist atmospheric air strongly supports the view that the IR continuum absorption, and probably similar absorption at longer wavelengths, is due to huge populations of electrically-neutral water clusters that are present in near-Gaussian size distributions in the vapor. These neutral water clusters exist in the vapor (as they do in liquid water) in equilibrium with much smaller populations of their water ions. Therefore, the water ions in the vapor have populations proportional to the IR-absorbing neutral clusters. Much can be learned about both species by carefully studying the electrical conductivity of moist air. These studies have shown that in the presence of electric fields, fine water droplets and finely structured water films on surfaces at higher RH are prime sources of water clusters in the vapor. The electric fields do not have to be large; those usually found in the earth's

troposphere (0.5-1.0 V/cm) are adequate for ion production from fine droplets and suitable moist surfaces.

The variability of the IR continuum absorption intensity arises from many factors. In a given electric field, the most important factors are vapor RH, the attainment of equilibrium, and the fineness or "quality" of droplets and surface water films. Bulk liquid water produces few ions directly from its surface, but evaporation of monomers and neutral clusters is a prerequisite for increased RH, which leads to the formation at higher RH of droplets and water films on surfaces in the vapor. The behavior of the liquid water surface, which forms the liquid/vapor interface, is very poorly understood even by the experts who study it; this behavior accounts for water's unusual physical properties including its very low saturation vapor pressure and is closely related to the nearly complete hydrogen bonding that exists in liquid water. It appears that many similarities exist between the electrical properties of liquid water and its vapor. Evidence that this is true includes our ability to accurately model the temperature dependence of the vapor IR continuum absorption by using the temperature dependence of the equilibrium constant (ion product) measured for the dissociation into ions of liquid water. The dissociation into ions of neutral water clusters in the vapor can be studied by using adiabatic expansion cloud chambers to grow droplets on neutral clusters and their ions large enough for optical detection. Once corrections are made for the phase density, the relative populations of water ions and neutral clusters thus measured in the vapor agree with those measured in liquid water.

The IR continuum absorption at any wavelength is limited due to size distribution clusters that have the proper size, configuration, and population to absorb there. Clusters of sizes n = 2 to 45 can exist in the vapor under various conditions. Therefore, the inference that the total population of all clusters in the vapor can be deduced by IR absorption measurements at a single wavelength is almost certainly false. For example, IR absorption attributable to the water dimer near $\lambda$ = 10 $\mu$m says nothing about absorption by clusters of other sizes and configurations at other wavelengths.

Recent research[6] also supports the view that the extent of molecular clustering in water vapor may be far greater than previously supposed. At a given temperature, some maximum number of equilibrium ions, and no more, can be produced in saturated (100% RH) atmospheric air regardless of how energetic the humidification process (e.g., if boiling water is used for humidification). This could occur because most water molecules in the vapor are clustered under such limiting conditions.

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# APPENDIX A

## NEW ELECTRICAL MEASUREMENTS OF ATMOSPHERIC MOIST AIR

The electrical conductivity of moist atmospheric air has been measured using a newly designed cell with a large electrode area; exceptional precautions were taken to eliminate surface leakage currents and other sources of experimental error. This design evolved from generations of earlier designs,[9,22-24,27,28] with which insulator leakage was studied in detail to determine how it could best be eliminated.

The new cell consists of 40 plates, comprising two inter-leaved sets of 20 plates each. These planar aluminum plates are 26.5 $cm^2$. Either set of plates can serve as the cell anode or cathode; measurements are independent of polarity. The total plate area and separation of 0.66 cm imply a capacitance of 3.7 nF, which was confirmed by measurements using an impedance bridge. Each set of plates is supported by four threaded stainless steel rods that pass through small holes in the sides of a lucite box (Figure A-1). The rods, which allow for electrical connection, are supported outside the box by 39-cm high PTFE pillars with sharply-pointed bases resting on PTFE shims. All insulators are enclosed within two vertical air ducts that have a common flow of warm air (typically ~ 60 °C and <15% RH) from a 600W air blow dryer (Figure A-1), therefore, avoiding possible surface films of water on the PTFE pillars. Pressure in these ducts slightly exceeded pressure within the box so that escape of moist air through the 1.3-cm diameter holes was prevented. The current through the cell was not changed by either operation of the air dryer or a small fan inside the box that could be used to circulate the moist air at a velocity of ~ 1 m/s. The insulator leakage resistance could always be maintained at >$10^{12}$ ohms regardless of the RH of the air in which the large electrodes (plates) were immersed within the box. Therefore, very sensitive, precise measurements of electrical conductivity of moist air within the box could be made using this apparatus. Humidification by a variety of techniques was possible; some are discussed below and in the figure captions.

The following results were among those obtained:

• At constant bias voltage and, therefore, constant electric field strength, conductivity $\sigma$ increases strongly with RH; in fact, $\sigma \alpha s^{13}$, where s = % RH/100 (the saturation ratio), at RH >70% and $\sigma \alpha s^{7-8}$ at RHs <70%.

• The conductivity of moist air is constant only for $E_b < E_b^*$, where $E_b^*$ is a critical cell bias at a given RH; for $E_b > E_b^*$, Ohm's law is invalid, and the conductivity increases with field strength at constant RH.

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- Under nonequilibrium conditions (e.g., if humidification is carried out by boiling water within the box), hysteresis can occur in σ about equilibrium values.
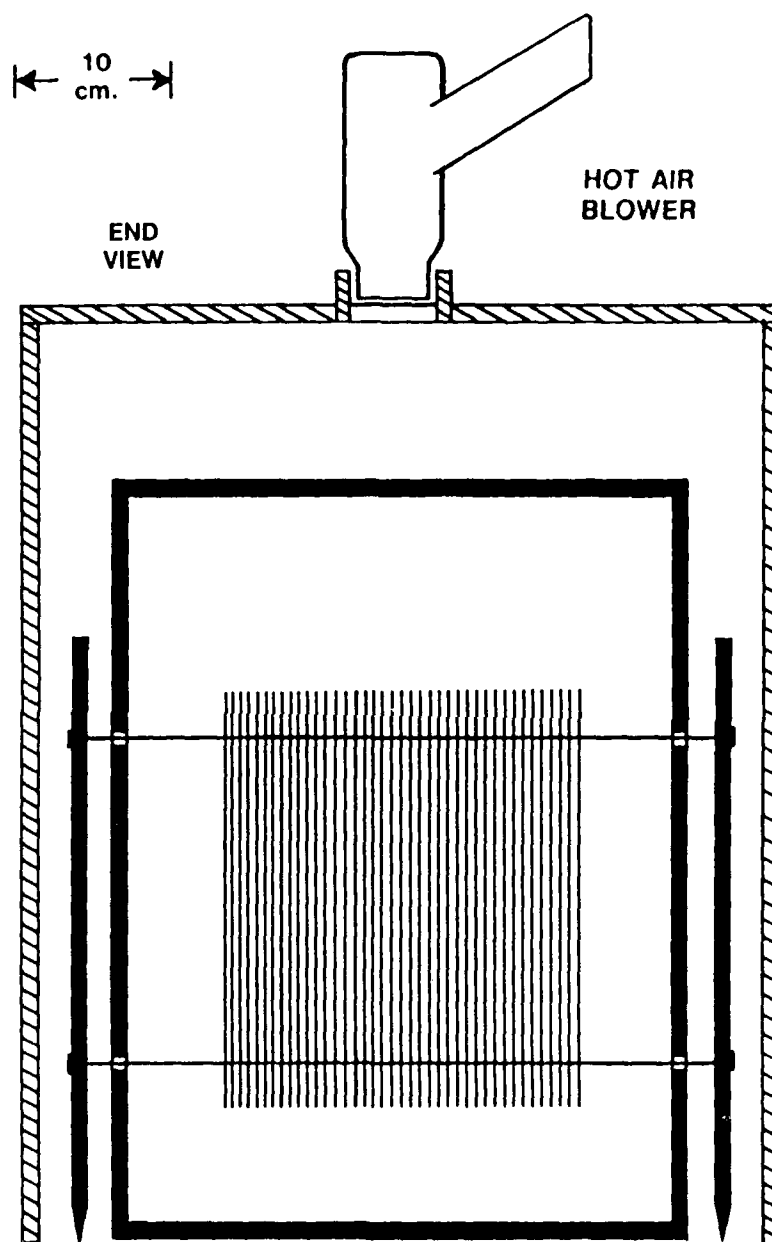
Figure A-1. Experimental Apparatus, Schematically Showing Cell Plates in Box with Threaded Stainless Steel Support Rods Passing Through Holes in Box Side Walls to Insulators in Vertical Warm Air Ducts Outside Box; 600W Blow Dryer Shown at Top.

The presence in moist atmospheric air of water ion species such as $(H_2O)_n^\pm$, where n is of the order 8-12, has long been accepted.[29] Recent mass spectrometric studies[31] of these and other water ions confirm their presence in water vapor in near-Gaussian distributions whose mean sizes at a given temperature depend upon humidity as $\sim \sqrt{s}$ (equation 2). In the case of these two polarities of water ion, one with charge $Z_+e$ and mobility $\mu_+$, and the other with charge $Z_-e$ and mobility $\mu_-$, the current density $\underline{j}$ in the cell is given by:

$$\underline{j} = \sigma \, E_b/L, \quad \sigma = Z_+e\mu_+I_{cc+} + Z_-e\mu_-I_{cc-}$$

where $I_{cc+}$ and $I_{cc-}$ are the number densities of the respective polarities of ions in the vapor, and L = 0.66 cm is the cell electrode separation. Therefore, $E_b/L$ is the electric field strength (volt per centimeter). In dry air, a typical ion density is $I_{cc} \sim 10^2/cm^3$. With $I_{cc+} = I_{cc-} = 10^2/cm^3$, $Z_+ = Z_- = 1$, and $\mu_+ = \mu_- = 1.55$ cm/s $(V/cm)^{-1}$, it follows that $\sigma = 2.4 \times 10^{-15}$ $(A/cm)(V/cm)^{-1}$. Then, if $E_b/L = 100$ V/cm, the current through the electrode area of 27,388 $cm^2$ is 0.067 nA. Measured currents in humid air exceeded this value by factors of 1000 or more near saturation, indicating that $I_{cc}$ was in the range $10^2-10^5$ $cm^{-3}$ and that it increased strongly with RH; in fact, $I_{cc} \propto s^{13}$ at these higher RH. Typical data are shown in Figure A-2.
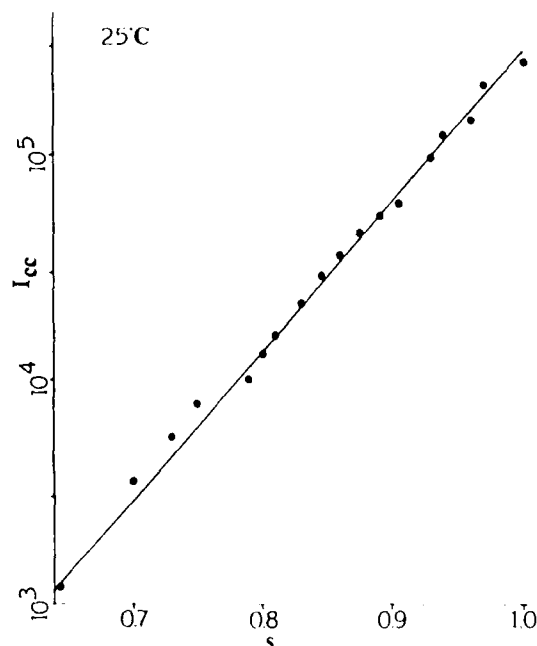


Figure A-2. Equilibrium Data from New Cell Showing Ion Density per Cubic Centimeter of Moist Air, $I_{cc}$, Versus Saturation Ratio, s = % RH/100, for Air at 25 °C Humidified by a Cool Water Fog from an Ultrasonic Nebulizer. The electric field strength was 600 V/cm.

Humidification by nebulized cool water fog, as shown in Figure A-2, gives equilibrium data. Humdification by evaporation of standing water, or by steam, gives similar data with some hysteresis about the $I_{cc} \sim s^{13}$ curve. During (dehumidification) data also follow this curve with some hysteresis. The effect of bias voltage $E_b$ or field strength $E_b/L = 1.5\ E_b$ on cell current is shown in Figure A-3, where the caption identifies other parameters, for several RH. At each RH, Ohm's Law is closely followed, and conductivity $\sigma$ is constant up to some critical cell bias voltage $E_b^*$, above which current and $\sigma$ increase with bias.
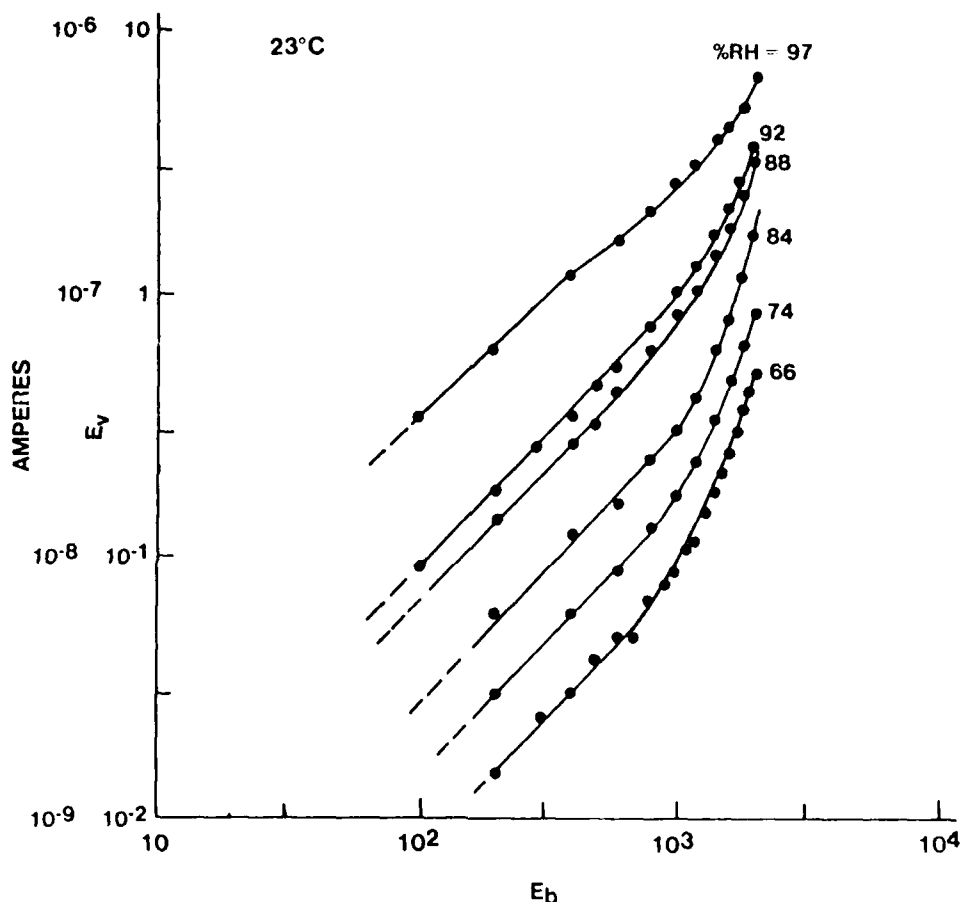


Figure A-3. Data from New Cell Showing Voltage E, Measured Across an 11 $\Omega$ Resistance in Series with the Cell and with a Source of DC Supply Voltage $E_b$ (Abscissa). The cell current, calculated in amperes, was always directly proportional to the ion population $I_{cc}$.[22,27] Data is typical of about 100 experiments. Note rapid rise of curves with increasing RH, corresponding to increasing thickness and activity of fine surface water films on cell plate (electrode) surfaces. See text for details.

The ion densities measured here range from those produced by cosmic rays and radioactivity[25,29] in dry or moderately humid air, to much larger values found in very moist and especially in saturated atmospheric conditions. Results from thousands of new data measured in about 100 recent experiments[6] led to the findings summarized in this report.

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# APPENDIX B

## THE IR CONTINUUM ABSORPTION: SAMPLE CALCULATIONS USING RESULTS OF THE NEW ELECTRICAL MEASUREMENTS IN APPENDIX A

If $\rho_v$ and $\rho_L$ are the densities of the vapor and liquid phases of water, respectively, then phase density correction of equation 6 in the text gives:

$$\text{(vapor)} \quad I_{cc} \sim 2 \sqrt{K_w} \, N_{cc} \, \rho_v/\rho_L \qquad\qquad \text{(B-1)}$$

Because $\rho_v = p_w M/RT_k$, and $\rho_L \sim 1.0$, it follows that:

$$\text{(vapor)} \quad I_{cc} \sim 2 \sqrt{K_w} \, N_{cc} \, p_w M/RT_k \qquad\qquad \text{(B-2)}$$

where

$p_w$ = water vapor partial pressure in Torr (mm Hg)

$M$ = molecular weight

$R$ = gas constant 62,360 $cm^3$-mm Hg/K g-mole

$T_k$ = Kelvin temperature

Using equation B-2, one can perform sample calculations to see if the hypotheses to this point are supportable by experimental data. An important factor determining the IR continuum absorption intensity is the fraction x of all water vapor molecules that are bound into clusters at any instant of time. For example, Suck et al.[14] estimated $x \sim 4 \times 10^{-4}$ under atmospheric conditions; they attributed the continuum absorption near $\lambda = 10$ μm solely to water dimers in the vapor. If the dimers are only the smallest clusters in a distribution (Figure in main text) of larger clusters, we would expect x, as calculated from measurements of water ions of all sizes in the vapor,[6] to be larger than $4 \times 10^{-4}$.

Combining equation 3 from the text with equation B-2 here and evaluating terms gives:

$$N_{cc} \sim I_{cc}T_k/p_w \exp (3578/T_k + 11.54) \qquad\qquad \text{(B-3)}$$

The IR continuum absorption due to $N_{cc}$ neutral water clusters per cubic centimeter of vapor, therefore, is proportional to the water ion population $I_{cc}$ per cubic centimeter as

measured by electrical conductivity[5] (Appendix A).  A first approximation of the mean size $n_\mu$ of the cluster distribution can be obtained from equation 2 in the main text.  Therefore, an average cluster will comprise ~ $n_\mu$ water molecules, and the total number of clustered molecules per cubic centimeter involved in the IR continuum absorption will be ~ $n_\mu \cdot N_{cc}$.  The total number of water monomers per cubic centimeter of vapor $N_{1_{cc}}$ is:

$$N_{1_{cc}} = p_w N_A / RT_k \qquad\qquad (B-4)$$

where $N_A$ is Avogadro's number, and the other terms are defined for equation B-2.  From equations B-3 and B-4, the cluster fraction, x, in the vapor is:

$$x \sim n_\mu N_{cc}/N_{1_{cc}} \sim n_\mu I_{cc}(T_k/p_w)^2 \exp(3578/T_k - 32.17) \qquad (B-5)$$

The vapor pressure $p_w = s \cdot p_w^o$, where s (the saturation ratio) = % RH/100, and $p_w^o$ is the saturation vapor pressure (Torr) at temperature $T_k$.  For example, at 25 °C, equation B-5 gives:

$$(25\ °C) \quad x \sim 3.3 \times 10^{-6}\ I_{cc}/(s)^{3/2} \qquad\qquad (B-6)$$

From Figure A-2, Appendix A, $I_{cc} \sim 10^3$ at 25 °C for s ~ 0.65.  Therefore, the cluster fraction under these conditions for clusters of all sizes in the population is x ~ $6.3 \times 10^{-3}$, in good agreement with the fraction x ~ $4 \times 10^{-4}$ estimated by Suck et al.[14] for the dimer alone under atmospheric conditions. Dimers and trimers in the cluster population would absorb near $\lambda = 10$ μm (equation 5 in the main text); whereas, larger clusters would absorb at wavelengths $\lambda > 10$ μm.  Because a cluster of size n will absorb $10^3$–$10^4$ times more strongly than n water monomers in the vapor at $\lambda = 10$ μm,[33] a fraction of dimers x = $4 \times 10^{-4}$ would account for about as much adsorption as would the overwhelming majority of all water monomers at this wavelength.  But from Figure A-2, Appendix A, at 25 °C, $I_{cc} \sim 3 \times 10^5$ at saturation humidity (100% RH).  Therefore, from equation B-6, x ~ 1; this would indicate that the water vapor was entirely clustered under conditions of vigorous water generation from an ultrasonic nebulizer that produced a thick fog of fine water droplets between the cell plates[6] and finely-structured water films on the cell-plate surfaces.

In repeated experiments,[6] it was found that the maximum ion population $I_{cc}$ for 100% RH at a given temperature could not be exceeded no matter how much additional energy was inputted to the system.  Nebulized fogs gave very reproducible data like those of Figure A-2, Appendix A, but maximum $I_{cc}$ values at 100%

RH could not be exceeded even if, for example, water was vigorously boiled into the test box from several sources simultaneously. Except for a small positive dependence of $I_{cc}$ upon temperature that was noted in boiling experiments, humidification even as vigorous as this produced no further ions. These observations could be explained if there were no further source of clusters (and hence ions) under these conditions because all water molecules in the vapor were already clustered (i.e., $x \sim 1$) in the electric field between the cell plates. If such extensive clustering in water vapor is possible, especially in the presence of dense, fine, water droplet clouds, this would explain how errors as large as $10^4$ can occur, due to continuum absorption, between measured values of atmospheric IR transmission and those computed from monomer line models that do not take cluster absorption into account.[1]

These sample calculations appear to support the hypotheses presented in this report. They provide evidence that the extent of molecular clustering in water vapor may be far greater than previously supposed.